

AD-A152 876

GAS PHASE ION-MOLECULE CHEMISTRY OF CARBON NITROGEN AND  
OXYGEN COMPOUNDS(U) COLORADO UNIV AT BOULDER DEPT OF  
CHEMISTRY C H DEPUY ET AL. 29 JAN 85 ARO-16004.11-CH  
DAAG29-82-K-0025

1/1

UNCLASSIFIED

F/G 7/4

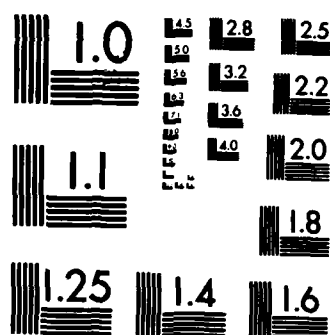
NL



END

FORMED

DTG



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 16004.11-CH ARO 18667.15-CH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Gas Phase Ion-Molecule Chemistry of Carbon, Nitrogen and Oxygen Compounds		5. TYPE OF REPORT & PERIOD COVERED Final: Oct. '78-Dec. '84
7. AUTHOR(s) Charles H. DePuy and Veronica M. Bierbaum		6. PERFORMING ORG. REPORT NUMBER 12
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Colorado Boulder, CO 80309		8. CONTRACT OR GRANT NUMBER(s) DAAG29-79-G-0012 DAAG29-82-K-0025
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N/A
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 1/29/85
		13. NUMBER OF PAGES 11
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.
---

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA
--

18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.
--

19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Flowing Afterglow, Trimethyl phosphite, methane imine, Selected Ion Flow Tube, silyl anions, aza allyl anion, Reactivity, phosphide anion, sulfides, Mechanism, nitrite esters, electron affinity, Thermochemistry, sulfur dioxide, (cont'd)
--

20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The gas phase reactions of nitrogen, silicon, sulfur and phosphorus organic compounds with anions have been investigated using the flowing afterglow technique. Studies have been made which compare mechanisms by which first and second row elements react with anions. New methods for the generation of specific anions in the gas phase have been developed. A variety of new types of gas phase ions ( $\text{PH}_2^-$ , $\text{R}_5\text{Si}^-$ , $\text{C}_3\text{H}_2\text{NO}_2^-$ , etc.) have been prepared and their chemical reactions studied.
--

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD-A152 876

DTIC FILE COPY

DTIC  
ELECTE

APR 29 1985

S D

Keywords included

ARO 16004.11-CH  
ARO 18667.15-CH  
ARO Report No. 12

GAS PHASE ION-MOLECULE CHEMISTRY OF CARBON,  
NITROGEN AND OXYGEN COMPOUNDS

FINAL REPORT

CHARLES H. DePUY  
VERONICA M. BIERBAUM

January 29, 1985

U. S. ARMY RESEARCH OFFICE

Contract Nos. DAAG29-79-G-0012  
and DAAG29-82-K-0025

UNIVERSITY OF COLORADO  
BOULDER, COLORADO 80309

APPROVED FOR PUBLIC RELEASE  
DISTRIBUTION UNLIMITED



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

85 4 00 185

TABLE OF CONTENTS

## Summary of the Research Program

A. Statement of the Problem Studied . . . . .	3
B. Summary of the Most Important Results . . . . .	3
C. ARO Sponsored Publications . . . . .	9
D. Participating Scientific Personnel . . . . .	11

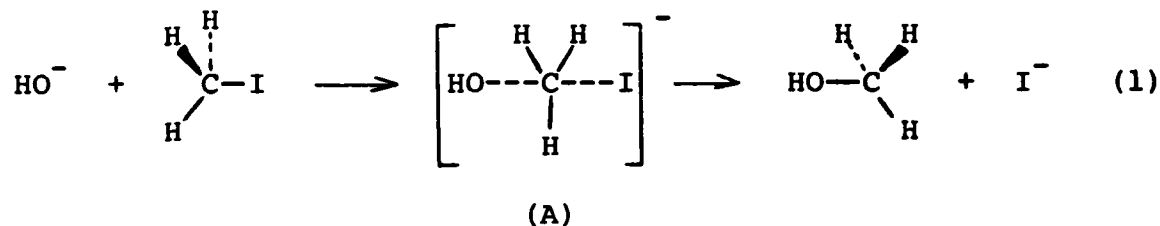
## Summary of the Research Program

### A. STATEMENT OF THE PROBLEM STUDIED

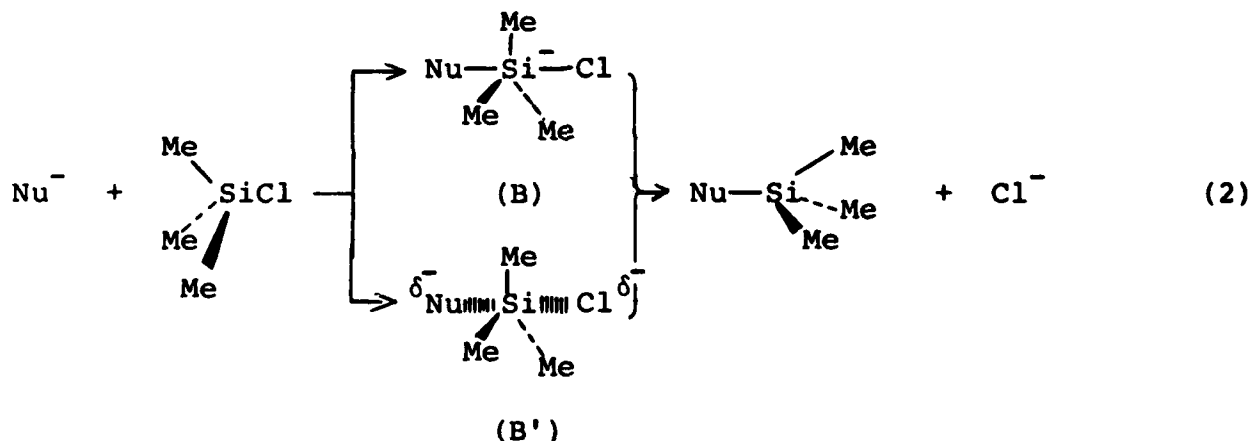
Our main interest in this work was to investigate the mechanisms by which first and second row elements, carbon, oxygen and nitrogen among the former, silicon, phosphorus and sulfur among the latter, react with nucleophiles. A related, secondary objective was to investigate the gas-phase ion chemistry of highly reactive compounds such as peroxides and nitro compounds. Our approach was to examine reaction rates and products for a number of neutral reagents reacting with anions at room temperature in the gas phase. The instruments used were a flowing afterglow (FA) and a selected ion flow tube (SIFT).

### B. SUMMARY OF THE MOST IMPORTANT RESULTS

Details of the techniques used, and an overall view of our gas-phase ion chemistry work is contained in three review articles.<sup>4,11,18</sup> We have made extensive studies of the reactions of silicon<sup>2,3,6,10,12,20</sup> and phosphorus<sup>15,21</sup> compounds with ions in the gas phase. One important, and basic, study was to compare and contrast the way an alkyl halide,  $\text{CH}_3\text{I}$ , and a silicon halide,  $(\text{CH}_3)_3\text{SiCl}$ , react with nucleophiles ( $\text{H}_2\text{N}^-$ ,  $\text{HO}^-$ ,  $\text{H}_2\text{P}^-$ ,  $\text{HS}^-$ , etc).<sup>10</sup> For  $\text{CH}_3\text{I}$  the process is the classical  $\text{S}_\text{N}2$  displacement reaction proceeding through a single transition state with Walden inversion (eq. 1).



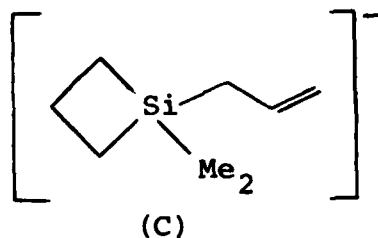
Because carbon can accommodate at most eight electrons in its bonding shell, (A) is a transition structure at the top of an energy hill. Second-row elements, for example Si, P and S, can in principle accommodate more than eight electrons and so the related structure could be either a transition structure (B') or a true intermediate (B). The difference is important because



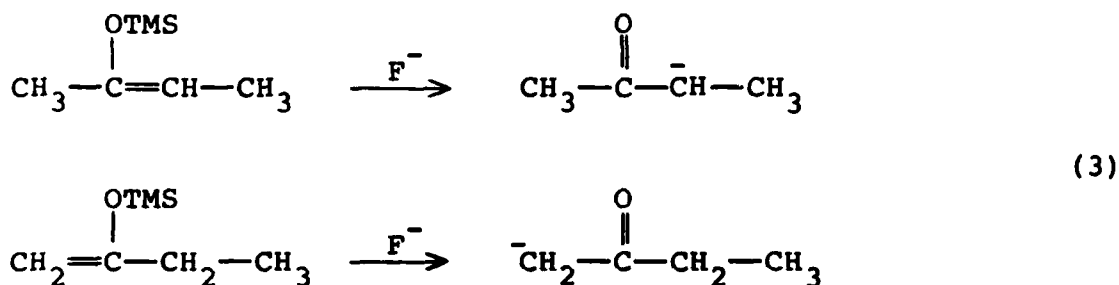
an intermediate can, in principle, be trapped or can undergo, for example, pseudorotation before being converted to product. We were able to show that the rates of reaction of the two halides differed profoundly in the way they responded to nucleophiles, and concluded that silanes did, indeed, react by way of a pentacoordinate intermediate.

In related work,<sup>6</sup> we studied cyclic silanes and showed that silacyclobutanes formed particularly stable pentacoordinate

ions, including a unique pentaalkylsilyl anion (C). We also



showed<sup>12</sup> how silyl derivatives of the isomeric enol forms of ketones can be used in the gas phase, as they are in solution, to generate regiospecific anions (eq. 3).

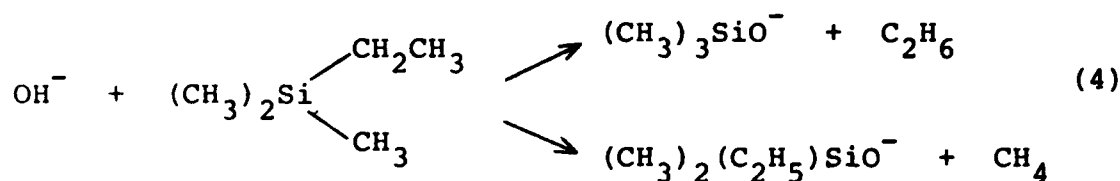


We made further use of silane chemistry to attack a problem of fundamental importance to all organic chemistry, the relative acidity of the alkanes.<sup>20</sup> While it is well known that a methyl group greatly stabilizes an adjacent carbocation ( $\text{CH}_3\text{CH}_2^+$  is much more stable than  $\text{CH}_3^+$ ), it is not known whether  $\text{CH}_3\text{CH}_2^-$  is much more stable than  $\text{CH}_3^-$ . Because of its stabilizing effect on a cation and based on its effect in solution, most organic chemists assume a methyl group will make an adjacent anion less stable. On the other hand,  $\text{CH}_3\text{O}^-$  is much less basic than  $\text{HO}^-$ , so in the alcohol series a methyl group appears to stabilize a negative charge. The problem is difficult to tackle experimentally because  $\text{C}_2\text{H}_5^-$  has never been prepared in the gas phase;



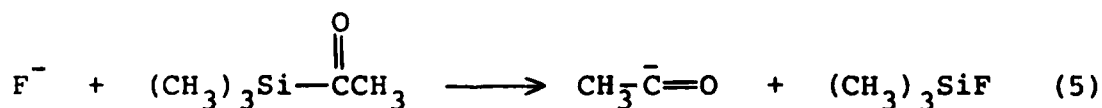
this anion is probably unstable with respect to electron detachment.

We discovered that alkyl silanes react with  $\text{HO}^-$  in the gas phase to form an alkane and a siloxide (eq. 4). In unsymmetri-



cally substituted silanes, we proposed that the relative amounts of alkane lost are a measure of the relative acidity of RH. For example, because ethane is lost less easily than methane, we believe that the ethyl anion (an intermediate) is more basic than the methyl anion and that, therefore, a methyl group makes an adjacent anion less stable. We are currently extending this study to other substituted silanes.

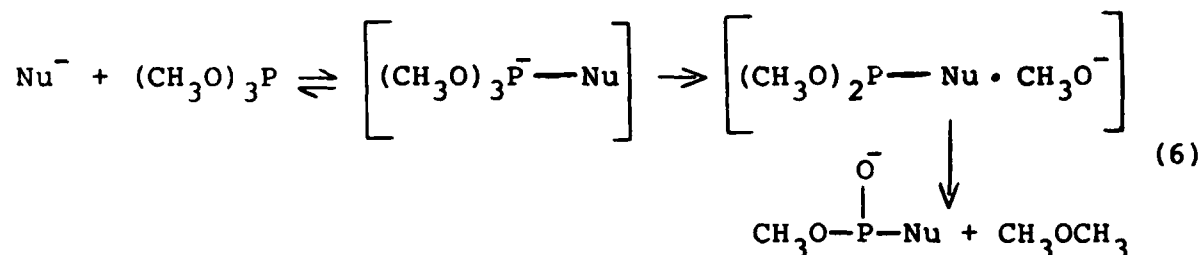
In recent, as yet uncompleted, work we have used silanes to generate the acyl anion (eq. 5). The gas phase chemistry of



this interesting and important anion can now be studied for the first time, and we also are determining (in collaboration with Prof. G. B. Ellison of this department) such crucial physical properties as its proton and electron affinities.

Phosphorus is next to silicon in the periodic table, and we have begun a study of the reactivity of phosphorus compounds. We recently published<sup>21</sup> the first general study of the ion

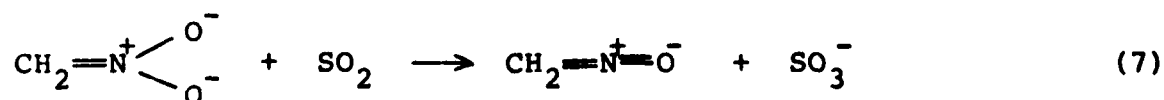
chemistry of trimethyl phosphite (eq. 6). Attack occurs



initially, and reversibly, on phosphorus, leading to displacement on one of the methyl groups.

In the study cited above, the phosphorus reagent served as the neutral electrophile. We also examined<sup>15</sup> the nucleophilic chemistry of phosphorus in  $\text{PH}_2^-$ , and compared it to that of  $\text{NH}_2^-$ , which lies just above it in the first row of the periodic table. The phosphide anion is less basic and less nucleophilic than the amide ion.

Nitrites and nitro compounds are among the most reactive organic compounds. We have examined the gas-phase ion chemistry of both types of compounds. In published work<sup>3,7</sup> we showed how nitrite esters undergo a variety of interesting and useful reactions with carbanions and other nucleophiles. In completed, but as yet unpublished work,<sup>22</sup> we have studied nitroalkanes both as electrophiles in their reactions with anions of various types ( $\text{NH}_2^-$ ,  $\text{HO}^-$ ) and as nucleophiles as their anions, formed by proton abstraction. These anions react primarily in the aci-form by oxygen transfer (eq. 7).



In other studies we have determined the electron affinity of  $\text{SO}_2$ <sup>14,19</sup> and of the important atmospheric radical  $\text{HO}_2^\bullet$ .<sup>5</sup> We developed a useful gas-phase ion synthesis of sulfides<sup>9</sup> and studied the formation and reactions of a series of nitrogen and sulfur anions.<sup>17</sup> We have also carried out collaborative studies of photodetachment with the Ellison group,<sup>16</sup> of vibrational energy disposal in ion-molecule reactions with the Leone group,<sup>1,8</sup> and of the mechanisms of reactions of some nucleophiles with phenyl acetate with the Nibbering and McIver groups.<sup>13</sup>

We have recently generated the novel methanimine anion ( $\text{CH}_2=\text{N}^-$ ) and the 2-azallyl anion ( $\text{CH}_2=\text{N}-\text{CH}_2^-$ ); the basicity, electron-binding energy and reactivity of these species have been studied.<sup>23</sup> We have also recently characterized the fragmentation processes for a variety of organic anions induced by exothermic addition reactions.<sup>24</sup>

## C. ARO SPONSORED PUBLICATIONS

1. Zwier, T.S.; Maricq, M. M.; Simpson, C. J. S. M.; Bierbaum, V. M.; Ellison, G. B.; Leone, S. R. "Direct Detection of the Product Vibrational-State Distribution in the Associative Detachment Reaction of  $\text{Cl}^- + \text{H} \rightarrow \text{HCl}(\text{v}) + \text{e}^-$ ," *Phys. Rev. Lett.*, **1980**, 44, 1050.
2. DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. "Gas-Phase Reactions of Anions with Substituted Silanes," *J. Am. Chem. Soc.*, **1980**, 102, 5012.
3. King, G. K. "Gas Phase Ion-Molecule Reactions of Alkyl Nitrites and Silanes," Ph.D. Thesis, University of Colorado, Boulder, Colorado, 1980.
4. DePuy, C. H.; Bierbaum, V. M. "Gas-Phase Reactions of Organic Anions as Studied by the Flowing Afterglow Technique," *Acc. Chem. Res.*, **1981**, 14, 146.
5. Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H. "Experimental Measurement of the Electron Affinity of the Hydroperoxy Radical," *J. Am. Chem. Soc.*, **1981**, 103, 6262.
6. Sullivan, S. A.; DePuy, C. H.; Damrauer, R. "Gas-Phase Reactions of Cyclic Silanes," *J. Am. Chem. Soc.*, **1981**, 103, 480.
7. King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. "Gas-Phase Reactions of Negative Ions with Alkyl Nitrites," *J. Am. Chem. Soc.*, **1981**, 103, 7133.
8. Maricq, M. M.; Smith, M. A.; Simpson, C. J. S. M.; Ellison, G. B. "Vibrational Product States from Reactions of  $\text{CN}^-$  with the Hydrogen Halides and Hydrogen Atoms," *J. Chem. Phys.*, **1981**, 74, 6154.
9. DePuy, C. H.; Bierbaum, V. M. "Gas-Phase Sulfur Anions: Synthesis and Reactions of  $\text{H}_2\text{NS}^-$  and Related Ions," *Tet. Lett.*, **1981**, 22, 5129.
10. Damrauer, R.; DePuy, C. H.; Bierbaum, V. M. "Reactions of Trimethylchlorosilane with Various Nucleophiles in the Gas Phase Using the Flowing Afterglow Technique," *Organometallics*, **1982**, 1, 1553.
11. DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. "Chemical Reactions of Anions in the Gas Phase," *Science*, **1982**, 218, 955.
12. Squires, R. R.; DePuy, C. H. "Flowing Afterglow Studies of the Reactions between Negative Ions and Trimethylsilyl Enol Ethers. Regiospecific Generation of Gas Phase Enolate Ions," *Org. Mass Spectrom.*, **1982**, 17, 187.

13. Kleingeld, J. C.; Nibbering, N. M. M.; Grabowski, J. J.; DePuy, C. H.; Fukuda, E. K.; McIver, Jr., R. T. "New Insight into the Mechanisms of Reactions between Some Anionic Nucleophiles and Phenyl Acetate in the Gas Phase," *Tet. Lett.*, **1982**, 23, 4755.
14. Grabowski, J. J. "Studies of Gas Phase Ion-Molecule Reactions Using a Selected Ion Flow Tube," Ph.D. Thesis, University of Colorado, Boulder, Colorado, 1983.
15. Anderson, D.R.; Bierbaum, V. M.; DePuy, C. H. "Gas-Phase Chemistry of  $H_2P^-$ ," *J. Am. Chem. Soc.*, **1983**, 105, 4244.
16. Oakes, J. M.; Jones, M. E.; Bierbaum, V. M.; Ellison, G. B. "Photoelectron Spectroscopy of  $CCO^-$  and  $HCCO^-$ ," *J. Phys. Chem.*, **1983**, 87, 4810.
17. Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. "Gas-Phase Synthesis and Reactions of Nitrogen- and Sulfur-Containing Anions," *J. Phys. Chem.*, **1984**, 88, 1389.
18. DePuy, C. H. "SIFT-Drift Studies of Anions," in M. A. Almoester Ferreira (ed.), *Ionic Processes in the Gas Phase*, New York, D. Reidel Publishing Company, 1984, pp. 227-241.
19. Grabowski, J. J.; Van Doren, J. M.; DePuy, C. H.; Bierbaum, V. M. "Flowing Afterglow Studies of the Electron Affinity of  $SO_2$ ," *J. Chem. Phys.*, **1984**, 80, 575.
20. DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. "Relative Gas-Phase Acidities of the Alkanes," *J. Am. Chem. Soc.*, **1984**, 106, 4051.
21. Anderson, D. R.; DePuy, C. H.; Filley, J.; Bierbaum, V. M. "Gas-Phase Chemistry of Trimethyl Phosphite," *J. Am. Chem. Soc.*, **1984**, 106, 6513.
22. Carrigan, K. E. "Reactions of Simple Nitroalkanes in the Gas Phase," M. A. Thesis, University of Colorado, Boulder, Colorado, 1984.
23. Kass, S. K.; DePuy, C. H. "Gas Phase Ion Chemistry of Azides: The Generation of  $CH_2=N^-$  and  $CH_2=N=CH_2^-$ ," *J. Org. Chem.*, submitted for publication.
24. DePuy, C. H. "Fragmentation of Organic Anions Induced by Exothermic Addition Reactions," *Org. Mass Spectrometry*, submitted for publication.

## D. PARTICIPATING SCIENTIFIC PERSONNEL

Charles H. DePuy, Professor of Chemistry, Principal Investigator.

Veronica M. Bierbaum, Senior Research Associate, Co-Principal Investigator.

David Anderson, Post-doctoral research associate.

Stephen Barlow, Post-doctoral research associate.

Kathleen Carrigan, Graduate Student; M.A. awarded, Aug., 1984.

Jonathan Filley, Graduate Student.

Joseph Grabowski, Graduate Student; Ph.D. awarded, May, 1983.

Gary King, Graduate Student; Ph.D. awarded, July, 1980.

Matti Maricq, Post-doctoral research associate.

Robert Squires, Post-doctoral research associate.

Sally Sullivan, Post-doctoral research associate.

Jane Van Doren, Graduate Student.

**END**

**FILMED**

**5-85**

**DTIC**